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Emerson,
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1886
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- Oxidation in the Aromatic Series.

A Thesis presented for the Doctorate
by - W. D. Emerson.

As work done in the Johns
Hopkins University, under the Direction of
Professor Ira Remsen.

April, 1886.

57 353

- Table of Contents -

Historical Introduction	1
Oxidation with Potassium Permanganate	2
Purpose of the work	3
Oxidation of Potassium Lysine Sulphonate	4
Oxidation of Pure Lysine Sulphonate	5
Bearing of results from above	6
Oxidation of Lysine	7
Bearing of result from above	8
Oxidation of Mono Nitro Mesitylene	9
Oxidation of Mesitylene Sulphonic Acid	10
Oxidation of Mesitylene Sulphonate	11
Summary	12

1

- Oxidation in the Chromic Series -

Historical Introduction -

In the year 1867 Beilstein and Knapp
found that the nitro group was oxidized
by means of the chromic acid mixture the
result being a nitrolic acid. In
combining this with the oxidation of the hy-
drocarbon itself in which case a nitrolic
acid is readily obtained, they were struck
with the change in conduct due to the
substitution of the nitro group, they found
further that there were a number of cases
reported in chemical literature which seemed
comparable to this one, nitrobenzene being
oxidized to nitrolic acid,
while trinitrobenzene under the same condi-
tions was completely stable, and the

conducts itself like nitroxybenzene yielding a colorless neutral substance which is entirely withstood the action of the chromic acid mixture. From these facts they were led to the conclusion that the entrance of negative elements or radicals into a hydrocarbon rendered it more stable towards oxidizing agents. The fact that the relation of the substitution products of xylene was not at the time understood and the examples chosen will show that they did not connect the location of the substituting groups, but believed that their presence gave the hydrocarbon as a whole greater stability towards oxidizing agents.

In 1871, Fittig⁽²¹⁾ called attention to the fact that the benzene ring, generally, distinguished itself from the corresponding meta and para compounds in their conduct towards potassium dichromate.

not isobutamic acid - instead of exhibiting characteristic oxidation products they are entirely inert. We seemed to think this difference was due to the greater instability of the ortho compounds, as he mentions among the ~~compounds~~ ~~which~~ ~~are~~ ~~less~~ ~~stable~~ phthalic acid, which he says distinguishes itself from the isomeric acids by its great instability towards the chromic acid mixture.

~~From the results of the work~~
of an investigation on barium isobutyrate
~~and its salts~~. The question was to determine
the acid was to oxidize the corresponding
toluene sulphinic acid - for the purpose of
oxidation the crude product obtained by the
action of sulphinic acid on toluene consisting
of both the ortho and para acids was used, in
expectation that the ~~ortho~~ ~~compounds~~ would
be destroyed in accordance with the views of

It is not the same acid thus he obtained
pure. The potassium salt of the resulting
product however, on fusion with caustic
potash gave both peroxybenzoic acid, and
salicylic acid, and further on a series of the
oxidation products were obtained. It also
gave a relatively greater quantity of the
ortho compound. The facts which came out
in the course of the investigation must not
be confined to the case of the greater sta-
bility of the ortho compound, but that say-
ing if the ortho compounds were on the other
hand more stable. The more complete the
oxidation the greater the proportion of the
ortho compound was obtained. This was
on fusion with caustic potash passed over
the same acid. A final comparison
of the ortho and para tolune sulphonic
acids showed this to be the case - the or-
tho was oxidized with greater difficulty - but

is oxidized at all but is even entirely - a combination of the corresponding oxides leads to the same result.

The above work led to a series of investigations by Hansen, published in the American Chemical Journal, as to the influence of substituting groups on the oxidation of aromatic hydrocarbons. In the first of these "On the Oxidation of Substitution Products" he states the problem in the following manner as to "whether the influence of a substituting group situated in the ortho position with reference to a hydrogen atom is such as to bring about actually or virtually to bring about the formation of the residue into carboxyl by the action of air mixture." The compound first studied was α -xylene sulfonamide, CC1=CC=C(C=C1)S(=O)(=O)NC, and the main product of oxidation was also found to be a substituted

toluic acid in which the methyl group was ortho to the substituting group. All the previous cases of oxidation which bore directly upon this subject were then collected together, and from a consideration of them it appeared distinctly probable that in all cases in which the ortho methyl group had been protected from oxidation by the presence of the sulphonic group, and that was true only for the toluic acid series. This investigation showed further that the protection was not complete, as the oxidation extended slightly to the second methyl group giving a very small quantity of a dibasic acid.

The next step taken was to study the influence of a substituting group upon the hydrocarbon carbon situated in the meta position with reference to the sulphonic group⁽¹⁰⁾. Mesitylene sulphonamide was cho-

seen. The oxidation gave a comparison in which two of the methyl groups remained unchanged, but contrary to expectation an ortho methyl group had been oxidized in about half the time, indicating mesitylene and phthalate which showed itself to be very stable towards the chromic acid mixture.

In the oxidation of benzene derivatives it is due to the presence of the sulphonic group, as would seem probable since some facts indicate that ortho groups are nearer than meta or para, it would not seem unlikely that a difference would be found in the ease of oxidation of residues with negative groups situated respectively in the meta and para positions. As to whether this difference would be apparent was tried in a comparison of the relative ease of oxidation of meta and para toluene sulphonates⁽¹⁰⁾. And so far as can be seen the results are as follows.

groups conduct themselves in exactly the same manner.

It was now proposed to investigate the extent of this influence in the hydrocarbon residues situated in the ortho position or "Can these same groups protect ethyl methyl and even complex residues? How far does the protective influence extend? Is in other words if larger groups are protected, what is the largest which can thus be protected?" An answer was given to these questions so far as the ethyl group was concerned in the oxidation of *para*-diethyl benzene sulphonic acid the product obtained was sulphamine ethyl benzoic acid, showing that the sulphonamide group was capable of protecting a group at least as complex as ethyl from the oxidizing action. This was then extended to methyl groups by two conclusive experiments.

para-Cymene sulphonamide $\text{C}_6\text{H}_4(\text{SO}_2\text{NH}_2)(\text{CH}_3)_2$ gave *para*-

It was anticipated that the bromine would
group as complex as $\text{NO}_2\text{O}_2\text{O}_2$.

The single exception mentioned above
was the formation of mesitylene sulphamide by
oxidation of mesitylene sulphamide. This seems
at all the more remarkable as it had been
shown that mesitylene sulphamide
on oxidation with the chromic acid mixture
para-chloro or bromo mesitylenic acid; the same
seems probably to hold good for nitro mesitylene,
— pointed out by de Meijere²¹, since para-nitro mesi-
tylenic acid is obtained as a secondary product
in the formation of mono-nitro mesitylene and
on this basis has been assumed as an intermediate
in the formation of nitro mesitylene. It was consequently
desirable that the conjecture regarding nitro mesity-
lene should be confirmed or refuted. It
furthered light thrown on the strange conduct
of the sulphamide of mesitylene. With this ob-
ject in view a portion of the work given be-

ion now undertaken.

Oxidation with Potassium Permanganate in Alkaline Solutions.

In the work mentioned above, published in the year 1875, Ransom had tried to obtain ortho sulphobenzoic acid by oxidation of ortho toluidine sulphonic acid with the chlorine acid mixture, but as was stated the ortho compound when attacked at all was actually destroyed so that this method was abandoned, but more recently because the other sulphonic acid in potassium permanganate may yield more satisfactory results. A preliminary experiment, made with this salt in alkaline solutions showed that this took place easily; I shall soon commence the study of this reaction in detail. In the preceding year I had, in this regard, oxidized ortho toluidine with potassium acid but omitted all the necessary experimental application of this reagent. In the course of the oxidation the

sulphuric acid was obtained in small quantity; it
 this result from the oxidation of the recent
 sulphur group in the sulphuric acid it seemed
 likely that potassium permanganate would ox-
 idize the sulphuric acid into the same sulphuric acid. In one experiment
 experiment the result being almost quantitative
 of the sulphuric acid. It is also found that if
 some sulphuric acid is added to the potassium permanganate it
 will oxidize the chromic acid mixture
 mixture more or less to regular radicals were ox-
 idized with ease while with the chromic acid
 mixture they were destroyed. In 1858 in the re-
 port of the committee by Professor Robinson⁽¹¹⁾
 had pointed out a remarkable uniformity in
 the action of fuming caustic potash towards
 substituted hydrocarbons, in these cases the
 action was exactly the reverse of that which
 has gone for chromic acid, the other groups being

oxidized to carbonyl. The most prominent point of difference between this reagent and chromic acid was that one was alkaline the other acid, and it was established that potassium permanganate in alkaline solution acted more effectively upon chromic acid. It was naturally expected that the permanganate would be found to be more readily acted in its end-product to the alkaline reagent. This conclusion seemed to be justified by the work of Remsen and Palmer¹⁰ in a comparison of the readiness of oxidation of the sulphamides of toluene and that of Meyer and Baer¹¹ in the oxidation of cymene sulphinic acid. In the first it was found that the oxidation of the toluene sulphinic acid took place with greater ease than that of the cymene sulphinic acid. It was found that the reaction was more rapid in the presence of water than in the dry state, which was ascribed to the substituting group,

was now oxidized to carbonyl - which under
certain conditions is oxidized to
acid - thus the former group is not
unal chemically then was that the permanganate
oxidized in preference the ortho group.

It has now been shown in a num-
ber of cases, conducted itself like chloric
acid, so that up to this time nearly every fact
known seemed entirely in harmony with an earlier
conjecture of Reims^(?) that with acid oxidizing
agents negative substituting groups protected ortho hy-
droxyl residues, but with alkaline oxidizing
agents exactly the reverse was true, and it seemed that
this statement might now be made with a great
degree of confidence and Reims now says -
"As it is established with a fair degree of certainty
that acid oxidizing agents tend to transform
ortho groups and leave ortho groups unchanged, and
that alkaline oxidizing agents tend to transform
ortho groups and leave para groups unchanged..."

Meyer's¹⁸ statement as this generalization is not entirely warranted as he completely omits the doubt expressed in the words given above, as will be seen by a comparison. "Negative result: *Äthylgruppen, welche sich in der ätherischen Lösung nicht auflösen, sondern in Benzol löslich sind, sind in der ätherischen Lösung unlöslich und bilden in Benzol eine Lösung, welche in der ätherischen Lösung unlöslich ist.*" "Positive result: *Äthylgruppen, welche sich in der ätherischen Lösung auflösen, sind in Benzol unlöslich und bilden in Benzol eine Lösung, welche in der ätherischen Lösung unlöslich ist.*" "Negative result: *Äthylgruppen, welche sich in der ätherischen Lösung auflösen, sind in Benzol löslich und bilden in Benzol eine Lösung, welche in der ätherischen Lösung löslich ist.*" "Positive result: *Äthylgruppen, welche sich in der ätherischen Lösung auflösen, sind in Benzol unlöslich und bilden in Benzol eine Lösung, welche in der ätherischen Lösung unlöslich ist.*"

The work was continued and the results of the next investigation, undertaken a short time ago and not yet published [I obtained the results in a private communication from Professor Reimer] throw doubt upon the conclusion arrived at so far as potassium permanganate in alkaline solutions was concerned.

This was the oxidation of α -xylene sulphide

The baraxylene used was obtained from Kahlbaum, and almost entirely so-
luble in the water-soluble ether. The melting point of pure baraxylene-

acid, the reaction took place readily by shaking together, and after several minutes the mixture was completely dissolved, the whole was then diluted to four or five litres, neutralized with chalk, filtered, and evaporated to about one half a litre. Treated with potassium carbonate filtered from the precipitated calcium carbonate, and evaporated to dryness. A small part was converted into the anhydride the melting point of which showed the compound to be the potassium salt of the desired sulphonic acid.

Oxidation of Potassium Paraxylylene Sulphonate - A preliminary experiment showed that the oxidation was continuous, 50 grms. of the sulphonate oxidized with 2200 c.c. of potassium permanganate, 70 grms. to the litre, gave mainly sulphonic acid. The sulphonic acid was not attacked. The reaction showed that if a monobasic acid was formed it was attacked.

in the reaction. The reaction was carried out in a certain temperature was reached between the quantities of the two compounds. So that in order to prevent as much as possible the complete oxidation the permanganate was used in the reaction was allowed to take place more slowly. Very good results were obtained when the amount calculated to oxidize one methyl group was used.

82 gms of the sulphinate was added to a solution of 50 gms of caustic potash in 800 c.c. of water. the oxidation was performed in two three litre balloons flasks heated in the water bath.

the permanganate was added 100 c.c at a time, waiting each time until the previous addition was decomposed completely. This required about half an hour at the beginning and increased gradually up to more than an hour. The addition was stopped when the solution was filtered in all. The solution was filtered in

The product was crystallized with succinic acid and evaporated to dryness, the organic salts then extracted with 80% alcohol. This solution was concentrated to dryness dissolved in hot water, and on cooling crystals were deposited, these were filtered and dried, and the potassium and water of crystallization determined.

Found.	Calc. for $C_{10}H_{12}O_6$	Calc. for $C_{10}H_{12}O_6$
	$\frac{10 \times 12}{31}$	$\frac{10 \times 12}{31}$

II. (Dry salt) 19.29.

2676

There were but three possibilities - the succinic salt and the malonic salt or the succinic and the malonic salts. In order to determine a mixture of the succinic salt with one or both the other possibilities. The neutral potassium salt was treated with hypochlorous acid and barium chloride, and the barium and water of crystallization of the resulting salt determined.

	Found	Calc. in $C_{15}H_{12}O_2$	Calc. in $C_{15}H_{14}O_2$
H_2O	57.5%		
Bar. Diquat	26.00%	27.12%	27.15%

The distillate from the dist. above, quite well with a mixture of two parts of the unoxidized with one part of a salt of cuprous bromine acid. That the unoxidized salt was present, and in considerable quantity, was shown by fusing with caustic potash. The substance was sometimes very viscous with water, when it is an oil, crystallized and was not in acid, gave no color with ferric chloride. The substance was found to be para-xenol. A very small quantity of a compound which gave a red color with ferric chloride was obtained at the same time, but in all probability resulted from the oxidation of the para-xenol.

The distillate from the same mixture, after the substance was treated with caustic potash, was found to be

Table.

$$\text{CH}_3$$

73

A Blue Egg salt, 18.15°

15. 34.

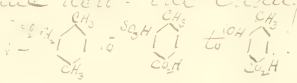
Don't

Accumulate. $C_{17}H_{35}O_2 + 2\frac{1}{2}H_2O$.

24.16 -

The Fe salt is extremely hygroscopic, which may account for the determination of the Fe being so low.

Another part of the potassium acid salt was heated with caustic soda, extracted with ether, evaporated to dryness, and fused with strong caustic soda over. Crystallized in needles. gave no color with ferric chloride, and melted 201-205. The acid was not entirely purified as the quantity was small. This was probably α -methylbenzoic acid. The melting point of which is according to Gerichten and Roseb¹¹ 206-207. The only other possibility was α -methylsalicylic acid, which melts at a degree lower, and gives an intense red color with ferric chloride. The oxidation product then was the sulpho-benzotoluic acid. The changes may be represented thus:



The ethereal extract after distillation showed only a very small residue the residue of which consisted of a substance which was insoluble in water but soluble in dilute acetic acid. It might not be found in the filtrate from the above. The filtrate was accordingly treated with barium chloride, and on heating a heavy white powder gradually settled causing violent bumping: this was entirely insoluble in water but moderately so in hydrochloric acid: from dilute acid it was completely dissolved. The barium and water of crystallization were determined with the following result.

	Found	Calculated $\frac{1}{2} \text{Ba} \cdot \frac{1}{2} \text{C}_2\text{H}_2\text{O}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$
H_2O	12.42.	12.50.
Ba. by salt.	2.88.	2.88.

The result shows barium sulphoterephthalate. The mother liquor on further evaporation gave an additional quantity of the same substance.

lignum with phosphorus pentachloride and ammonia the original amide was obtained, showing this to be the case. The mother liquor was no further investigated so in all probability it consists entirely of the unoxidized salt.

It was thought that perhaps the alkaline or acid nature of the substituting groups might influence the course of the reaction, the amide and this subjected to oxidation.

Oxidation of Para-Tylenesulfinamide.

The amide and the salt were dissolved in caustic potash and water in the proportions given above, and the oxidation carried on in the same manner.

600 C.C. of the permanganate were added through the hypodermic needle to the solution.

was killed, and on acidifying a precipitate
came down, very insoluble in water, and crys-
tallizing beautifully. It melted at about 270°
~~and on acidifying a precipitate~~

A portion was fused with caustic potash.
extracted with ether, evaporated, the residue, and
distilled with steam. A volatile acid passed
over, which crystallized exactly as the oxy. acid
obtained from the same material. The mother liquor
was evaporated to dryness, the residue was
fused with potash, which color was obtained

with ferric chloride, which disappeared on re-
crystallizing. The transformation may be rep-
resented thus
$$\begin{array}{c} \text{SiO}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \end{array} \xrightarrow{\text{SiO}_4} \begin{array}{c} \text{C}_6\text{H}_3 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \xrightarrow{\text{SiO}_4} \begin{array}{c} \text{C}_6\text{H}_3 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array}$$

The color observed may have been due to a slight im-
purity in the unoxidized anhydride, it being
also very insoluble. and on fusion with caus-
tic potash some pass easily into the ^{corresponding} ~~acid~~
~~acid~~ but not pureness was not suffi-
cient to perceptibly alter the melting point.

was precipitated gave, on further evap-
oration, a finely crystalline precipitate of ap-
parently homogeneous needles which did not melt
even above 300° . A determination of the po-
tassium and water of crystallization gave
results agreeing with the formula of potas-
sium di-sulphate.

	Found.	Calculated-
H ₂ O.	6.19	5.96
B. Dry salt.	13.74	13.77

The amide group had been converted into
the sulphonic acid group on oxidation of the
ortho methyl group - a change which has been
observed in a number of cases and is not
unusually ²⁰ common.

The above results are in accordance
with those of Remsen and Day, and show that in
these cases the MnO_4^- is not the MnO_2 .
manganate in alkaline solutions.

Chronic acid in oxidizing a group in the meta or para position to the substituting group in preference to one in the ortho position: but fails in that the oxidation extends very readily to the ortho group. Thus, it will be seen, seems exactly contrary to the facts firmly traced by Meyer for the sulphamide of cymene; however, if it could be shown that in cymene itself the meta group was more susceptible to the permanganate than the propyl, the apparent inconsistency could be explained. With this object cymene was subjected to oxidation.

Oxidation of Cymene

A specimen of cymene used was distilled, and only that portion taken for the experiment which boiled between 170° and 180°. 37 gms of cymene were oxidized using 22 gms of calcium peroxide in 375 cc. of water and 220 cc. of permanganate of 45 gms. to the litre. The oxidation was performed in two flasks with inverted con-

23
Towers, the vessels immersed in running water,
and all the permanganate added at the first.
The time required for complete fermentation
was about three days. The solutions were il-
luminated nearly neutralized evaporated to a small
volume and the acids precipitated with
hydrochloric acid. A preliminary examination
had shown that at least two acids were present,
one or all probably being obtained. The
acids obtained above were therefore converted into
the calcium salts hoping that the extreme
insolubility of calcium triphthalate would
give a good separation. From the most in-
soluble calcium salt, was obtained an acid
very insoluble in water, coming down in
an amorphous form, infusible and greenish.
By adding the soluble calcium triphthalate
acid. A pure acid was however not ob-
tained from the most soluble salt, the
melting point of the acid being about 100°C.

even after repeated crystallization the melting
 point and appearance however indicated α -
 isopropyl benzoic acid. on boiling this acid with
 dichromic acid a more distinctly soluble acid
 was obtained. melting at a lower indicating β -
 isopropyl benzoic acid. this was then boiled
 with very strong hypochloric acid for several
 times using the directions given by Meyer⁽²¹⁾ for con-
 verting the α -isopropyl or β -isopropyl benzoic acid into
 isopropyl benzoic acid. The acid obtained was
 extremely insoluble in water, and melted between
 240° and 260°, the isopropyl according to Meyer
 melting above 200° and 210°. The acid was converted
 into the barium salt, and the barium and
 color of crystallization determined.

	Found	Calculated for $(C_9H_9O_2)_2Ba + H_2O$
η_{sp}/c	3.7	3.7
Ba.	29.60	29.52

The product was not identical with the one pre-
 viously formed as stated by Meyer⁽²²⁾. but also

the product is a solid and apparently in
 a pure state. Quantities under the conditions
 given.

The mother liquor from which the acids
 were precipitated was extracted with ether
 and a very small quantity of an oily substance
 was obtained which on being recrystallized
 from water gave an acid with melting point
 such as to indicate impure α -hydroxypropionic
 acid. These results have been con-
 firmed by the work of M. L. H. and Blodgett⁽³³⁾ which
 has just appeared.

From this it will appear that the
 oxidation of amine sulphonide is conditioned
 at least by two circumstances, exactly contrary in
 their tendency, if we suppose that in this
 reaction, as in the case of the oxidation of
 amine sulphonide the substituting group
 affects the rate of reaction, then are
 the influence of the substituting group and

the relatively greater stability of the propyl group - but as shown the protection of an ortho group is very weak and may be actually reversed by the tendency of the permanganate to attack the ortho group in preference to the propyl group.

The action of oxidizing agents on substituted hydrocarbons cannot therefore be determined alone by their acidity or alkalinity, and perhaps not in any other very simple way - while it cannot yet be denied that the tendency of negative elements or radicals is to protect ortho groups from acid oxidizing agents and meta or para from alkaline, it is ~~very difficult~~ to limit the scope of a generalization in this case. It may however be seen among a number of conditions as would be indicated by the fact that the generalization holds for chromic acid and caustic potash while nitric acid and permanganate coming between in their action may be more influenced by other

autoxidation reactions. It is certain however that the nature of the group is influential and perhaps also the relative power of the oxidizer. But as to what the conditions are the present facts hardly warrant a conjecture.

Oxidation of Mono-Nitro-Nucitylene -

The feasibility of this oxidation was pointed out above. The following are the details of the work. The nitro-nucitylene was made according to the directions of Laccabue²⁷; - first made the dinitro-nucitylene, converted this into nitro-nucitylene by reduction with alcoholic ammonia, and finally purified. This was a very slow about one week being required to achieve nearly pure, mononitro. The mononitro was then oxidized to nitro-nucitylene by means of the Fieser reaction, distilled with steam and identified the product by its melting point. Fittig²⁸ had attempted the oxidation with the chromic acid mixture

but failed owing as he thought to the slowness
in the reaction. It was thought that this
slowness might be overcome by heating the
crystalline in acetic acid, heating with a
solution of chromic anhydride in acetic acid
and heating gently. 10 gms. of the monosilico-
polymer were heated in a solution of
chromic anhydride gradually added, waiting
each time until the pure green color indicating
complete reduction appeared. The reaction did not
take place at ordinary temperature, so the so-
lution was heated in the water bath to 60°C.
The addition was stopped when the pure green
color ceased to appear. The whole was then
diluted to a considerable volume with water,
a white precipitate settled, which was filtered
and washed. Recrystallized from water and al-
cohol. The product was an acid not readily sol-

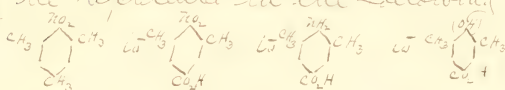
soluble in water. The melting point was not
 observed. A small amount of the substance was melt-
 ing at about 200° very distinct at $210-220^{\circ}$ cor and
 completely at 220° cor; recrystallization from
 water the melting point is the same.

Metaphenic acids are readily separated by means
 of their various salts, the acid in hand was
 converted into the barium salt, and this sub-
 jected to recrystallization until only a very small
 quantity remained. The acid was then rebe-
 come from a hot solution of this portion of
 the salt, and the acid was found to
 be essentially the same as before. The melting
 point given by Jacobson⁶¹ for the para-acid
 (which is the one obtained from the more in-
 soluble barium salt), is, when precipitated under
 these conditions, 170° cor and when precipitated in
 absolute alcohol 220° cor. Schmidt⁶² has pre-
 viously described this substance, and though
 he gives the melting points somewhat lower

These specimens were all found to melt at the upper limit - showed indications of melting as low as 200° ; he says however that even he is not sure about the purity. With the acid obtained here, the lower melting point was in no case first obtained, but it was noticed on allowing the specimen to cool in the capillary tube it did not solidify until the temperature was 100° or lower, and then was no variation observed in this, except in a few cases where it solidified at a point above the melting point and was probably due to imperfect fusion: for on again fusing and allowing to cool it solidified at $100-100,000$. If the specimen was cooled from 100° or in some cases as low as 80° , depending apparently on the conditions of cooling, it melted at $100-100,000$. The lower melting point of this acid as given by Schmitz. There was no variation in this respect the substance was

that it could not be purified satisfactorily; the
 product was the result of a mixture in
 the melting point which for the pure acid is
 115°, according to the literature.

They are represented in the following manner:



Oxidation of mesitylene sulphonic acid-

It now having been shown that in meso mesity-
 lene sulphonic acid the two sul-
 phonic groups are protected from chemie acid, it
 was found to be possible to oxidize the meso mesity-
 lene sulphonic acid, which as stated above
 gives mesitylenic sulphonic acid. If this were due to
 the activity of the sulphonating group, the cor-
 responding sulphonate salt should give the same
 result as obtained for the other negative groups;
 the sulphonic acid was therefore subjected to
 oxidation. 20 grams of mesitylene were dissolved
 in 200 grams of fuming sulphuric acid (18.5%)

with twice the volume of water, and cooled

Barium dichromate was then added in small
lumps the action not taking place at ordinary
temperatures. On heating the mixture in a water
bath, and when once started took place very vio-
lently; 100 grms. of potassium dichromate were added
only a few minutes being required to complete the ox-
idation. The whole was then diluted to several litres,
and the precipitate of barium sulphate and chromate
chloride filtered from the precipitated sulphate
and chromate treated with carbon dioxide to
precipitate excess of barium, filtered and evaporated
to dryness. On heating the residue no evidence could
be found of a sulphomethylene acid. The
methylene sulphonic acid having been active-
ly burned. The oxidation was then repeated
raising the temperature from 60 to 100°, and
allowing the oxidation to proceed very slowly,
several hours being required for completion;

from the residue.

The residue was next treated
free by heating running sulphuric acid with
about half its volume of mesitylene, and sep-
arating the sulphuric acid which crystallized
out on standing, by absorbing the sulphuric
acid with porous plates. The dry sulphuric
acid was then treated with phosphoric
acid, and treated with chlorine anhydride in
acetic acid; oxidation took place slowly at
ordinary temperatures, and a very small quan-
tity of a white precipitate settled; this was
filtered off, dissolved in water, neutralized with
barium hydroxide, treated with carbon dioxide,
filtered, and evaporated to dryness, the residue
treated with phosphoric acid, and with
ammonia: but no anide was obtained.

The acetic acid solution was evaporated as
far as could be in the water bath and

acted in the same manner, and in this case
no oxide obtained.

The sulphide was ~~prepared~~ with
the oxide, and oxidized exactly as the acid
except that it required to be heated to about 70
degrees ~~centigrade~~ ^{centigrade} before the
the action was stopped, a slight excess of
acetic acid added to the solution boiled, and
filtered from the precipitated oxide of chromium
an acidifying a fine crystalline precipitate was ob-
tained; the melting point showed it to be quite pure
sulphamide of methylene. The oxidation was re-
peated with this portion and on treating as above
no precipitate was obtained. ~~Later~~ ^{Later} apparently the
oxide had been entirely inner though no evolution
of gas could be observed. but by connecting the flask
with a vessel containing lime water, it was shown
that a gas came off slowly giving a precipitate in
the lime water solution. The results therefore of
the investigation ^{on this last point} were entirely negative.

Ann. *Reichs-Anstalt für Chemie.*

A. *American Chemical Journal.*

Am. *American Journal of Science.*

B. *Beiträge der Deutschen Chemischen Gesellschaft.*

Z. *Zentralblatt für Chemie.*

(1) Ann. 1810.

(16) B. 1810.

(2) Z. 1811.

(3) Ann. 1812.

(18) *Beiträge der Deutschen Chemischen Gesellschaft*
Ann. 1812.

(4) A. 1813.

(19) B. 1813.

(5) A. 1814.

(20) A. 1814.

(6) A. 1815.

(21) Ann. 1815.

(7) A. 1816.

(22) B. 1816.

(8) A. 1817.

(23) B. 1817.

(9) A. 1818.

(24) Ann. 1818.

(10) Ann. 1819.

(25) Ann. 1819.

(11) Ann. 1820.

(26) B. 1820.

(12) Ann. 1821.

(27) Ann. 1821.

(13) A. 1822.

(28) Ann. 1822.

(14) A. 1823.

(29) Ann. 1823.

(15) A. 1824.







